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THE FORMATION OF SMALL PARTICLES AND AGGREGATES IN THE RHINE ESTUARY

by

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CONTENTS

I. INTRODUCTION

During several cruises in 1976 to 1979 in the Southern Bight of the North Sea and the eastern Channel, water samples were collected (EISMA & KALF, 1979) and the nature of the suspended particles was examined directly on board with an inverted microscope as commonly used in plankton studies. This allows inspection of the particles in their natural state down to a size of approximately 5 micron. The surveys were made in January and February; so hardly any living plankton was found: only in a few samples were some living diatoms present. The non-living particles consisted of subrounded mineral grains (quartz, feldspar, clay minerals, also some calcite) and aggregates. Coarse particles ($\gtrsim$70 μm) were almost exclusively aggregates. Exact counting, especially of the finer size fractions, was not possible on board but it was estimated that in the surface water *ca* 50 to 80% of the particles were aggregates and the remainder mineral grains. In the near-bottom samples *ca* 30 to 60% of the particles were aggregates. The aggregates consisted of small mineral grains and brownish floccules, held together by a usually brownish-greenish substance. Aggregates without mineral grains, which were assumed to be pure organic matter, were rare, at least in the sizes above a few microns.

Also rare were particles of recognizable organic origin such as diatom frustules. It follows that those formed during spring, summer and autumn are either deposited or dissolved before January.

Particles smaller than *ca* 5 μm cannot be examined very well with the inverted microscope, so they were centrifuged off during the cruise of 1979 in order to avoid masking of the smaller particles by the larger ones, and examined with a transmission and scanning electron microscope in combination with a Link micropobe. For the TEM a drop of water with suspended particles was pipetted directly on a Formvar-carbon coated copper grid and after drying examined in a Philips EM 300. For the SEM (Cambridge 150), part of the sample was filtered through a 0.4 μm Nuclepore filter. In the size fraction < 5 μm, apart from artificially produced chains of seasalt particles, mainly five types of particles were present: mineral grains (usually angular and flat), more or less round, often open aggregates (with the particles glued together by some structureless greenish or brownish substance which is lost when the samples are treated with H_2O_2 and therefore is taken to be organic matter), very small chain-like aggregates <0.5 μm, floc structures of variable shape (often containing some small minerals), and very small particles (<0.5 μm) consisting entirely of structureless material (presumable organic matter as they disappear easily when the electron beam is focussed on them). The mineral grains were either opaque or greyish, sometimes nearly transparent with little contrast, and were found to contain only Si, only Ca or combinations of Mg, Al, Si, K, Ca and Fe, indicating the presence of quartz, calcium carbonate and clay minerals or feldspars. Besides the five types of particles, some bacteria and a few particles showing organic structures and consisting of quartz or calcium carbonate were found. The smallest particles observed were in the order of 0.02 μm. There were no clear differences between the particulate matter in the Dutch coastal water, the "Channel Water" in the centre of the Southern Bight and the English coastal water, but the floc-type of particle was probably more numerous in the Dutch coastal water samples. Although the TEM and SEM analyses give only qualitative results, on the whole by far the most particles were more or less round, often loose aggregates with less single mineral grains and some chain-like aggregates, flocs and small (organic?) particles.

The average (apparent) density of the suspended particles larger than 0.5 to 1.0 μm can be determined from the total weight and volume of the particles (Fig. 1) and from the following relations:

$$\bar{\rho} = \frac{M_s + M_w}{V_s + V_w} = \frac{M_s + M_w}{V_{tot}} = \frac{M_s + (V_{tot} - V_s)\,\rho_w}{V_{tot}}$$

and:

$$V_s = \frac{M_s}{\rho_s}$$

where $\bar{\rho}$ is the average density of the particles, ρ_s, M_s and V_s the average density, mass and volume of the solid part of the particles, ρ_w, M_w and V_w the average density, mass and volume of the water in the particles and V_{tot} the average total volume of the particles. The material in suspension is a mixture of inorganic mineral particles and organic matter. The samples collected in 1976 to 1979 contained virtually no opal so that the inorganic part of the particles has a density of about 2.65, the organic part a density near to 1.1. For the samples collected in 1976, 1977 and 1978 the ignition loss at 520° C was found to be, on the average, 14%, 22% and 13% respectively. The ratio between ignition loss and organic carbon has been found to be 1.6 ± 0.6 (MEADE *et al.*, 1975) and the ratio between organic matter and organic carbon *ca* 2 (BOUGIS, 1974). The average organic content was thus 18% in 1976, 27% in 1977 and 16% in 1978. From the average weight (M_s) of the material >0.5 μm (filtered on a Nuclepore filter), the average volume (V_{tot}) of the material >1 μm (as determined with a Coulter Counter; Fig. 1; data after EISMA & KALF, 1979) and with the average organic content, ρ_s, V_s, V_w and $\bar{\rho}$ can be calculated. The mean value for $\bar{\rho}$ for all samples is 1.97, with a minimum of 1.14 and a

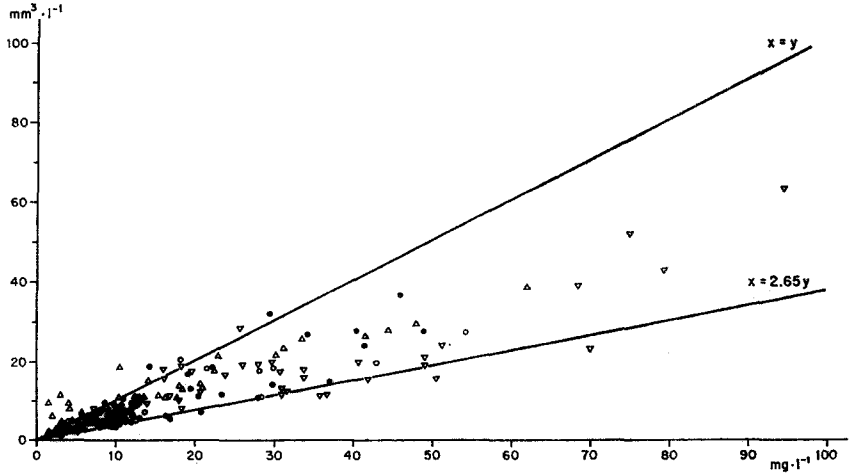

Fig. 1. Relation between total dry, salt-free weight ($mg \cdot l^{-1}$) and volume ($mm^3 \cdot l^{-1}$) for suspension samples collected in the Southern Bight and the eastern Channel in 1976 to 1979; the 1976 samples (●) volume was calculated for the size fraction 3 to 125 μm, for the 1977 (▽), 1978) (△) and 1979 (○) samples for the fraction 1 to 128 μm.

maximum of 2.65. Mean water content of the particles is 27%, but water content can be up to 90% or 0. The large variation is primarily due to the mixed character of the particles but is also caused by imperfect knowledge on the relations between ignition loss, content of organic carbon and content of organic matter.

Aggregation of suspended particles may occur in several ways (*cf.* ZABAWA, 1978) but estuaries may be especially important sites because of (a) the high particle concentrations and more frequent interparticle contact, (b) the usual presence in or near the estuary of relatively high amounts of bottom fauna and plankton both of which can aggregate particles, and (c) the change in particle charge and the removal of metals, especially iron, from solution at or near the contact of fresh water and more saline water (BURTON, 1976), which may result in flocculation and aggregation of particles. Moreover, the estuaries of the Scheldt and the Rhine and, further north, the Wadden Sea play an important part in sediment trapping along the Belgian-Dutch coast. This is specially true for the Rhine estuary because the entrance has been artificially deepened to make room for large ships, allowing a larger influx of suspended material along the bottom. About 9 to 15 million tons (dry weight) of suspended material is yearly supplied to the Belgian-Dutch coast whereas in the Rhine estuary alone ("Waterweg") yearly about 7 to 10 million tons is dredged and more than 70% of this is dumped into the coastal sea. The contribution of the Rhine river itself is less than 2 million tons per year (EISMA & KALF, 1979). It follows that a large percentage of the particles in suspension along the Belgian-Dutch coast may have been in estuarine conditions at least once. It was decided therefore to study the principal estuaries and suspended matter samples were collected in the estuaries of the Rhine (in 1977 and 1979), and the Scheldt (in 1977) and in the western Wadden Sea (in 1977). Particle volume size distributions, determined with a model TAII Coulter Counter, were approximately log-normal (EISMA & KALF, 1979) with, in the western Wadden Sea and at low salinities in the Rhine estuary (2 to 5‰ S), a strong admixture of particles of 1 to 3 μm which was absent in the Scheldt estuary (Fig. 2). During the period of sampling, size distributions along the Belgian-Dutch coast were also approximately log-normal. Influx of suspended material from the sea, therefore, accounts for the distributions found in the Rhine estuary and the Wadden Sea except for the strong admixture of fine particles at low salinity. Since the admixture was predominantly present at low salinities and particle or aggregate formation is likely to occur at or near the contact of fresh water and more saline water, some mixing experiments were carried out with Rhine water and filtered sea water.

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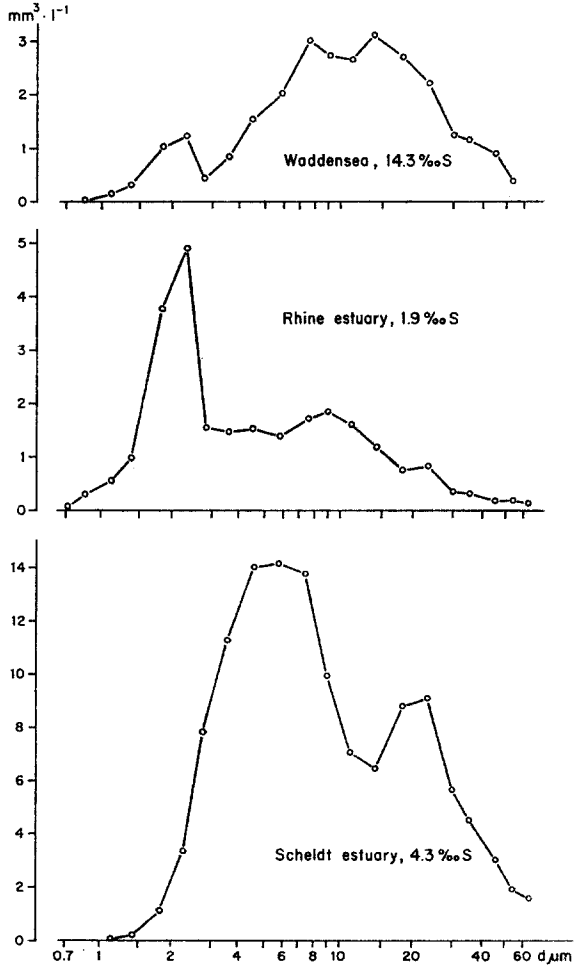


Fig. 2. Size distribution of suspended matter in samples collected in the Wadden Sea (NZ-58) at 14.3‰ S, in the Rhine estuary (NZ-57) at 1.9‰ S and in the Scheldt estuary (NZ-50) at 4.3‰ S.

Rijkswaterstaat at Hoek van Holland for their assistance in collecting fluid mud samples in the Rhine estuary and to Mr S. J. van der Gaast, Mrs R. Gieles-Witte and Mrs A. Visser-Hensey for their assistance in

sampling and in the laboratory. We would also like to thank Mr C. Gerssen and the crew of the R. V. Aurelia for their assistance on board and the drivers Mr J. Visser and Mr S. Gieles for their assistance in collecting and analysing Rhine water.

II. PARTICLE FORMATION IN THE RHINE ESTUARY

The mixing experiments were made in January 1977 (in the absence of living plankton) and repeated in January 1978, January 1979 and in May and June 1979. The Rhine water was collected just upstream of

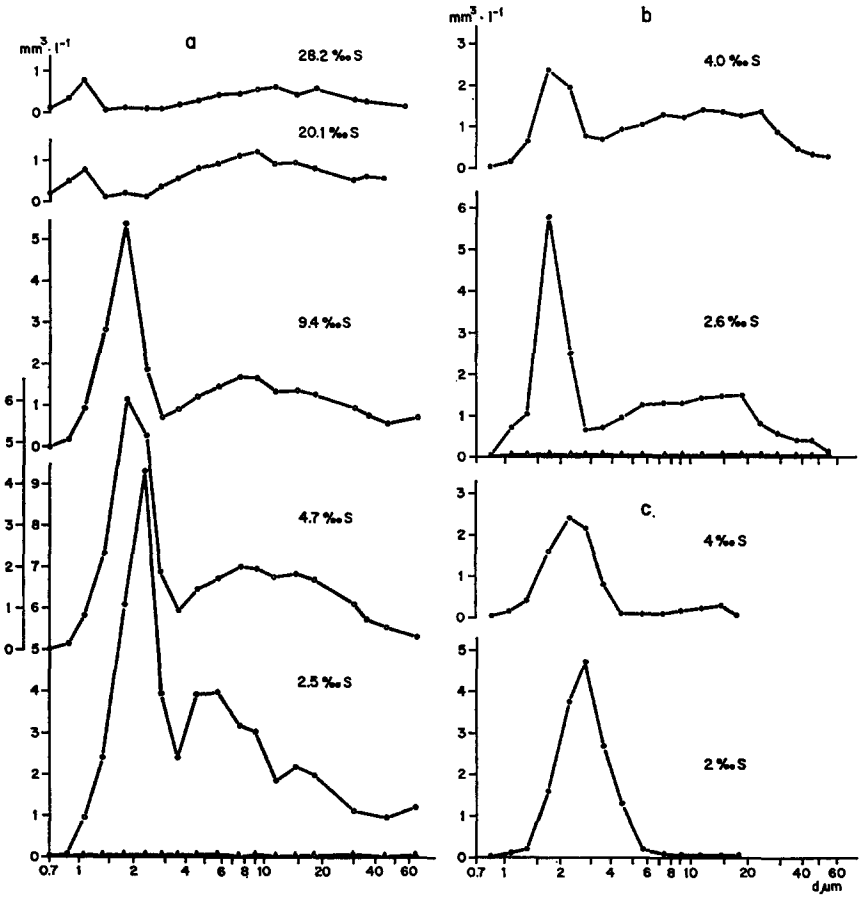


Fig. 3. Size distribution of suspended matter in mixtures of river water and filtered sea water, together with blank of filtered sea water (△). a. Rhine water mixtures of 28.2, 20.1, 9.4, 4.7 and 2.5‰ S. b. Zaire water mixtures of 4.0 and 2.6‰ S. c. Mixtures of 4‰ and 2‰ S of filtered Rhine river water with filtered sea water.

Rotterdam, the mixtures with filtered sea water were made directly after sampling and in the mixtures particle size was measured within 15 to 30 minutes. In 1977 a mixing series of *ca* 2‰ S up to *ca* 30‰ S was made, in 1978 and 1979 only low-salinity mixtures of 2 to 5‰ S. The sea water was filtered through a 0.4 or 0.2 μm Nuclepore filter before mixing. All mixing experiments gave the same result in the form of a strong peak at 1.5 to 3.0 μm at low salinities, which is at the same place as the peak found in the samples from the Rhine estuary (Fig. 3a). This peak was also found when filtered river water (filtered over a 0.4 μm Nuclepore filter) was mixed with filtered sea water (Fig. 3c) or when distilled water was mixed with filtered or artificial sea water (Fig. 4). This indicates that the particles of *ca* 2 μm are formed on mixing by chemical precipitation and were not supplied from the river or from the sea. An interesting feature is that in the mixtures of higher salinity the size of the particles decreased to *ca* 1 μm, the peak at this size was

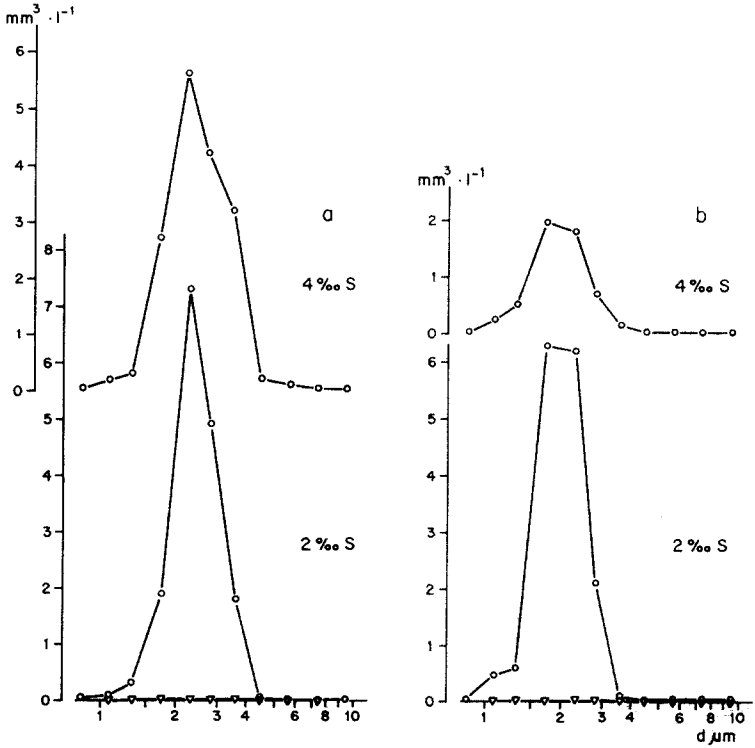


Fig. 4. Size distribution of suspended particles in 4 and 2‰ S mixtures of (a.) distilled water and filtered sea water, and (b.) distilled water and artificial sea water, together with blanks of filtered sea water or artificial sea water (▽) (control of distilled water by microscope showed only a few dust particles).

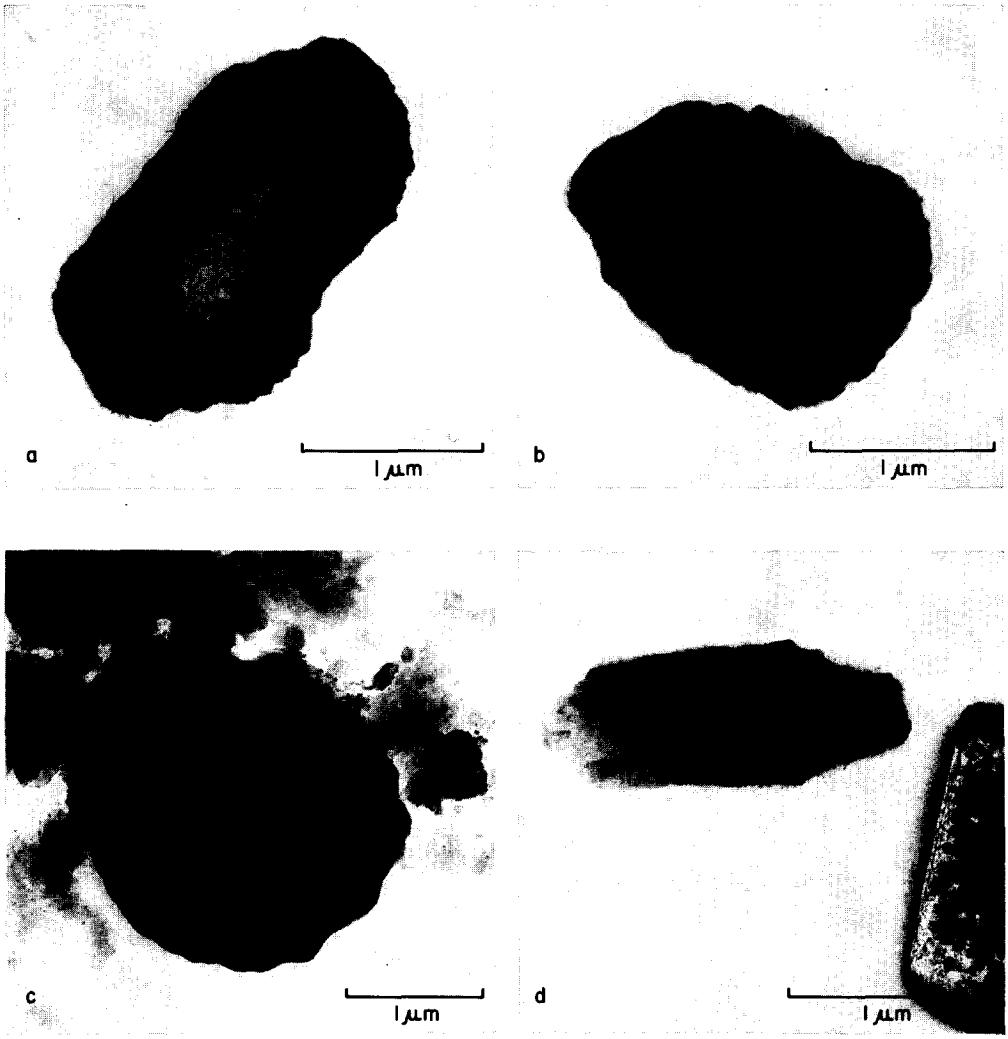


PLATE I

a. Oval particle of *ca* 2 µm from a 2‰ S mixture of filtered sea water and distilled water. b. Oval-round particle of *ca* 2 µm from a 2‰ S mixture of filtered river water and filtered sea water. c. Oval-round particle of *ca* 2.5 µm from the Rhine estuary at *ca* 1.2‰ S. d. Oval particle of *ca* 2 µm from the Rhine estuary at 2.3‰ S.

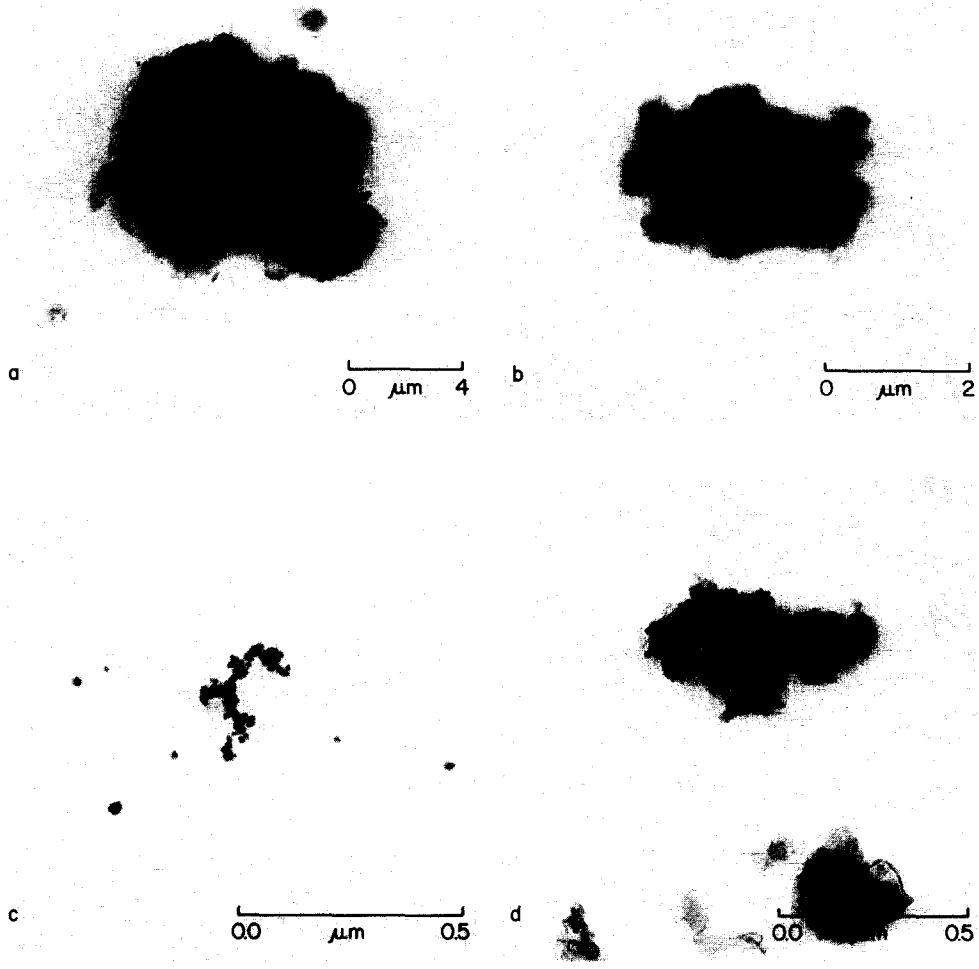


PLATE II

a. Round aggregate of *ca* 8 µm containing mineral particles in an amorphous (organic) ground mass. b. Aggregate of *ca* 3 µm. c. Chain-like aggregate of *ca* 0.28 µm. d. Aggregate of mineral particles in an amorphous (organic) ground mass of *ca* 0.5 µm.

low and a size-distribution was formed that is very similar to those found in the Dutch coastal water (*cf.* the 20.1‰ S mixture in Fig. 3a with samples NZ-1, NZ-3 and 79-10 in fig. 9 of EISMA & KALF, 1979).

From the river water, the estuarine samples and the artificial mixtures the size fraction >5 μm was centrifuged off and within several hours after taking the samples and measuring the size-distributions, the fraction <5 μm, left in suspension, was studied under an electron microscope. The same was done for filtered sea water and filtered river water. In 1979 this was repeated with an additional series of samples from the Southern Bight. In the mixtures as well as in the estuarine samples and in a sample collected just off the river mouth large numbers of oval to nearly round particles of 1 to 3 μm with typical radial streaks were found (Plate I). They were absent in the river water, the filtered river water and the filtered sea water. They were most numerous in the samples with a high peak around 2 μm (the artificial mixtures and the innermost samples from the estuary) and gradually decreased in number in samples of higher salinity. In the estuarine and nearshore samples the oval-round particles are sometimes covered with small flakes of other material (Plate I). This is most probably not artificially produced during sample preparation but the result of natural scavenging in the estuary: in the artificial mixtures of river water and filtered sea water numerous small flakes of the same type were found but the oval-round particles were not covered by them. In the artificial mixtures the oval-round particles dominated, while relatively few other particles of the same size were present (usually contamination with dust). In the samples from the estuary many other particles—mineral grains as well as aggregates—of approximately the same size were present with relatively few oval-round particles. In the samples from the Southern Bight above *ca* 20‰ S no oval-round particles were found.

In January 1978 no means for further identification of the particles were available: the water samples containing the fraction <5 μm as well as the EM grids with the oval-round particles were stored at 4° C. After 7 months the oval-round particles were still present, apparently unaltered, in the water samples but they had largely disappeared from the EM grids and Nuclepore filters. Using an EDAX system and later a LINK system the elementary composition of the oval-round particles was determined in the samples from 1978 as well as in freshly collected samples from 1979. They were found to contain chiefly Ca and S with sometimes additional amounts of Cl, K, Mg, P and in some cases detectable amounts of Fe, Si, Na and Al. The ratios with respect to Ca are given in Table I. The ZAF corrections were made using the procedure developed by YAKOWITZ, MYKLEBUST & HEINRICH (1973).

TABLE I

Element ratios of 1 to 2 μm particles formed at low salinities.

Elements	*Ratio*
Ca/S	1–7
Ca/Cl	> 12
Ca/K	> 28
Ca/Mg	>119
Ca/P	>140
Ca/Si	>300
Ca/Fe	>400
Ca/Al	>600
Ca/Na	>600

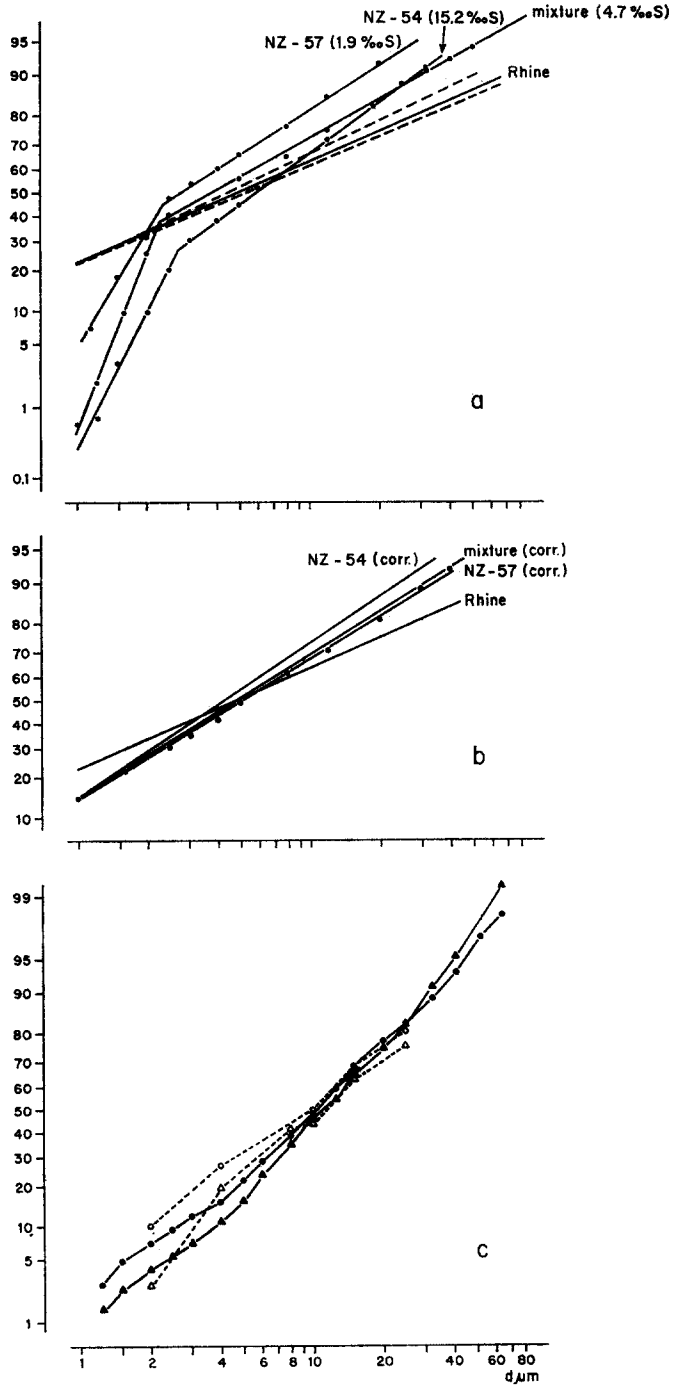
No difference in composition was found between the radial streaks and the lighter ground mass but in the central part of the particles the Ca/S and Ca/Cl ratios tend to be higher (22 to 192 and >96 respectively). The elementary composition suggests a complex of Ca^{++}, SO_4^{--}, CO_3^{--} and OH^- whereas the presence of small amounts of K, Mg, Al and Si indicate some inclusion of alumino silicates (presumably clay minerals). The particles contain water that can be boiled off under the electron microscope.

The oval-round particles are either natural and result from a purely inorganic chemical reaction of dissolved ions or inorganic complexes without any involvement of particles or colloids, or are artificial products of the EM technique and the Coulter Counter. The Coulter Counter may produce artificial results at salinities below *ca* 1.5‰ S because the conductivity of the water decreases. However, when samples at such low salinities are measured, the results become erratic and no artificial peaks appear, whereas calibration tests with particles of known diameter still give good results at *ca* 2‰ S. In artificial mixtures as well as in natural samples a peak around 2 μm has been found up to 20‰ S and often is also present (but much lower) at higher salinities in the Southern Bight and in the eastern Channel. The formation of an artificial peak in the Coulter Counter is therefore highly unlikely. The EM technique may produce artificial results because particles settle out and are dried during preparation of the sample. The drying also produces particles of sea salt in the shape of small cubes and sometimes elongated crystals clustered into irregular star-shaped or hand-shaped clusters. The sea salt particles are very unstable, since they contain much water that escapes when in the TEM they are heated by the electron beam. They are easily distinguished from the oval-round particles so there is no chance of confusion, but under the same circumstances the oval-round particles might be

artificially produced in low-salinity water. In samples with a high peak at *ca* 2 μm, however, comparatively large numbers of oval-round particles of approximately that size were found. A second indication that the oval-round particles are not artificial is that the peak at *ca* 2 μm was not found in the Scheldt estuary, where samples were measured down to 4‰ S. If the particles were artificial a peak should also have been found here at *ca* 2 μm. It can therefore be considered very likely that the oval-round particles are indeed formed in nature in estuaries during mixing with sea water. The absence of such particles in the Scheldt estuary may be related to the low oxygen content in the uppermost parts of this estuary which results in a different chemistry as compared to the Rhine, the Zaire and the Wadden Sea (BILLEN, SMITZ, SOMVILLE & WOLLAST, 1976).

III. AGGREGATE FORMATION

The (irregular) admixture of a fine size fraction of 1 to 5 μm in the Southern Bight and the eastern Channel is not explained by the formation of the oval-round particles in estuaries. These particles were not found at salinities higher than 20‰ S and probably are not stable in sea water. Aggregates of *ca* 2 μm may be formed on the contact of fresh water and saline water since aggregates of about that size were present in the artificial mixtures of river water with filtered sea water, but also much coarser aggregates are found (Plate II). A comparison of size frequency distributions of suspended matter from the Rhine (results of 4 samples from just above Rotterdam determined by settling, all being very similar) with those in an artificial mixture of 4.7‰ S of Rhine water and filtered sea water (determined with the Coulter Counter) and in two estuarine samples (NZ-57, collected at 1.9‰ S, and NZ-54, collected at 15.2‰ S) is given in Fig. 5a. Size distribution determinations by settling and with a Coulter Counter give comparable results (BEHRENS, 1978, and trials made in our laboratory) but usually the pipette analysis gives a somewhat higher content of fine particles (usually between 2 and 8 μm; an example is given in Fig. 5c): a number of particles evidently has a lower fall-velocity than quartz spheres of the same size which is only to be expected when the average density of the supended particles is less than 2. Above 2.5 to 3 μm all size distributions in the Rhine river and estuary are approximately log-normal. In the Rhine the suspended material is even somewhat coarser than in the estuary. The curves given in Fig. 5a, however, are not entirely comparable because the Coulter Counter does not measure the amount of particles <1 μm. Through settling it was found that the estuarine samples contain 13 to 15% (weight) of particles <1 μm.


NZ - 54 (15.2 ‰S)
mixture (4.7 ‰S)
NZ - 57 (1.9 ‰S)
Rhine
a
NZ - 54 (corr.)
mixture (corr.)
NZ - 57 (corr.)
Rhine
b
c
d,µm

Correcting the curves of samples NZ-57 and NZ-54 for this amount and smoothing out the peak at *ca* 2 μm by assuming that it is due to the formation of the oval-round particles, we obtain the curves of Fig. 5b. For comparison also the data for the artificial mixture of 4.7‰ S were treated in the same way, assuming that in the mixture the fraction <1 μm was also 13 to 15%. The curve for this mixture than becomes almost identical with the curve for NZ-57. Also after making the corrections, the suspended material of the river is somewhat coarser than the suspended material in the estuary. If this is not due to local variations in particle size or to accumulation of fine particles in the estuary, it would point rather to breaking up of particles in the estuary than to particle formation.

The main difference between the river and the estuary is in the fraction <3 μm: the peak at *ca* 2 μm is absent in the river water and the fraction <1 μm decreases with *ca* 9% going from the river to the estuary. If this amount is formed into aggregates of different sizes, it will not be noticed: a few percent difference in several size fractions cannot be distinguished from local variations in particle size. If it is formed entirely into aggregates of *ca* 2 μm, the newly formed aggregates together with the particles of that size already present would account for *ca* 45% of the peak at that size, the remainder being the newly formed oval particles. This is still in agreement with the (qualitatively estimated) predominance of the oval-round particles in that size fraction; aggregate formation in this manner may also account for the peak at 1 to 3 μm found at higher salinities. It follows from this discussion that aggregation on the contact of fresh water and sea water plays only a limited part, if any, in particle formation, at least in the Rhine estuary. This may be a consequence of the pollution of the Rhine with salts, predominantly NaCl, $CaCl_2$ and sulphates which has raised the salinity of the river water in its lower reaches to an average of 0.61‰ S (maximum 0.91‰; RIWA, 1978). Aggregation caused by compression of the electrical double layer therefore may have occurred already far upstream from the estuary (POSTMA, 1967).

There are, however, other possible ways of aggregate formation, as

Fig. 5. Size distributions on log-probability paper of suspended matter in the Rhine estuary. a. Rhine water, 2 samples from the Rhine estuary (NZ-54 at 15.2‰ S and NZ-57 at 1.9‰; for sample locations see Fig. 6) and an artificial mixture of Rhine water and filtered sea water (4.7‰ S). b. Rhine water compared with corrected size distributions of the estuarine samples and the artificial mixture given in a.; the corrections involve subtraction of the peak at *ca* 2 μm and adding the amount of particles <1 μm as determined by settling. c. Comparison of particle size distribution of two Wadden Sea samples (collected in Texelstroom at *ca* 25‰ S and 26‰ S) determined by pipette analysis (○, △) and with a Coulter Counter (●, ▲). The range of variation is usually ±10% for both methods.

can be surmised from the multiple origin of the material in suspension in the Southern Bight and the eastern Channel as well as from the predominance of aggregates that are glued together by, presumably, organic material. Apart from flocculation on the contact of fresh and more saline water, aggregates can be the result of: (a) erosion of soils and consolidated fine grained deposits, (b) increased particle contact near to the bottom at high concentration of suspended matter, (c) still greater interparticle contact during temporary deposition (during calm weather or slack tide), (d) activity of organisms producing faeces, pseudo-faeces or secreting a mucous substance.

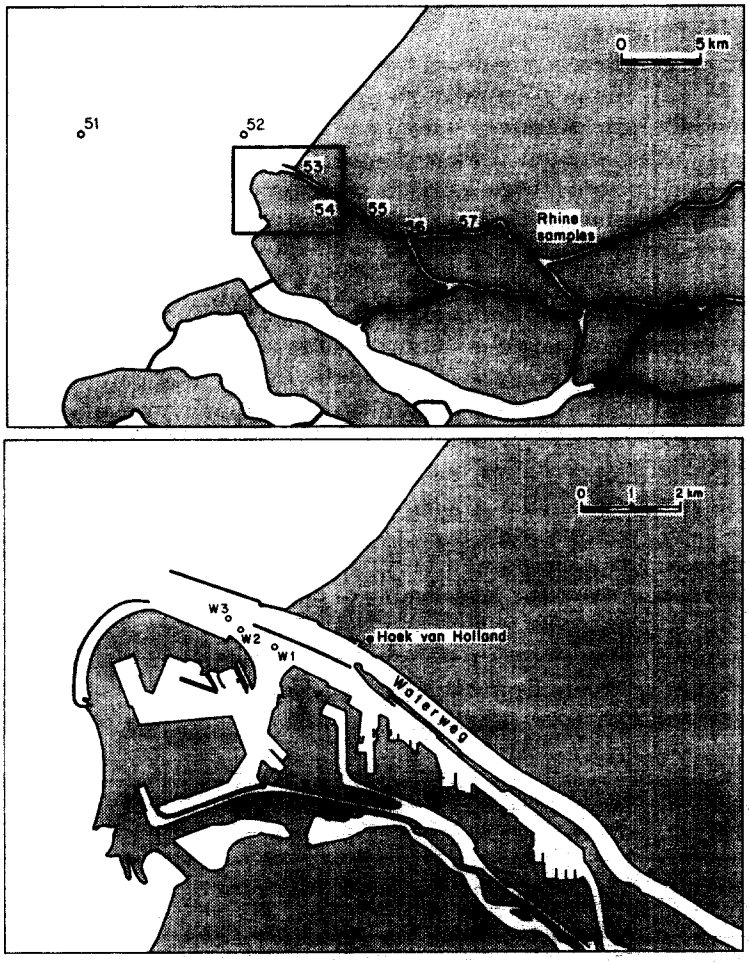


Fig. 6. Rhine estuary (Nieuwe Waterweg) with sampling stations NZ-51 to 57 (above) and W1, W2, W3 (below).

Still another possibility is that in estuaries aggregation occurs over a long distance and not particularly at the contact of fresh and saline water. MARTIN, JEDNACAK & PRAVDIĆ (1971), NEIHOF & LOEB (1972) and ASTON & CHESTER (1973) found that the negative charge on suspended particles gradually decreases with increasing salinity so that aggregation by electrostatic or Van der Waals forces may be extended over some distance (for a summary see BURTON, 1976). A gradual change would not show in Fig. 5; a more detailed comparison along the Rhine estuary (Fig. 6) of the relative amounts of particles in the separate size fractions (Fig. 7) indicates a gradual increase in the fractions between 5 and 20 μm with increasing salinity, and a marked increase in the amount of particles of 2.51 to 5.04 μm between *ca* 5‰ S and 9‰ S. If this is not caused by a break-up of particles >20 μm, and also not by size selection in the estuary (related *e.g.* to the inward transport of suspended material from the sea), this would be in agreement with aggregate formation along most or the entire length of the estuary.

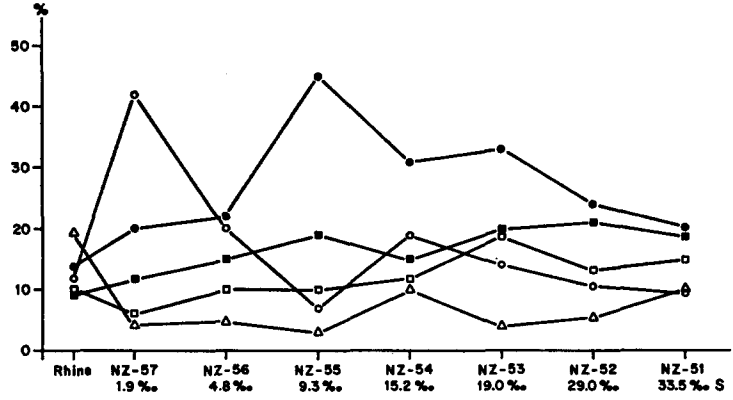


Fig. 7. Percentage of suspended particulate matter in separate size fractions (in $mm^3 \cdot l^{-1}$) at sampling locations (see Fig. 6) along the Rhine estuary; fractions of 1.26 to 2.51 μm (○), 2.51 to 5.04 μm (●), 5.04 to 8.00 μm (■), 12.7 to 20.2 μm and <30 μm (△).

It follows from the above discussion that the aggregates are likely to have been formed in different ways, which is also implied by the multiple origin of the suspended material supplied predominently from the Channel, from several rivers and from seafloor erosion with small additional amounts from the atmosphere, from coastal erosion and from primary and secondary production. The importance of organic matter for aggregate formation can be surmised from the fact that removal of organic matter by oxidation gives a strong peak at (usually)

ca 2 to 5 μm which cannot be reduced further by ultrasonic treatment (as was also found by McCAVE, 1979, for some samples off East Anglia) but that up to 16 minutes of ultrasonic treatment still leaves the aggregates partly intact so that usually a peak is formed at some intermediate size between the original peak and the peak formed after removal of the organic material (Fig. 8).

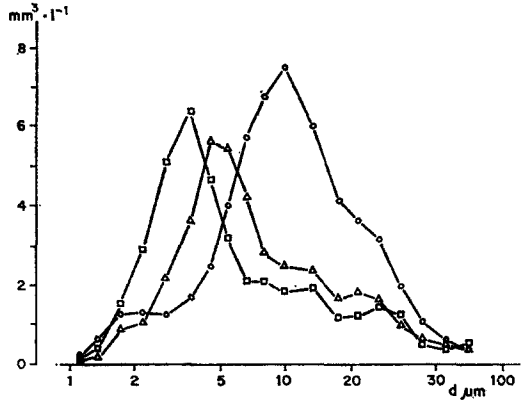


Fig. 8. Particle size distribution of suspended matter from the Dutch coastal water off Scheveningen after 4 minutes of ultrasonic treatment (△), after treatment with H_2O_2 (□), and directly measured on board (○).

IV. AGGREGATION AT HIGH PARTICLE CONCENTRATIONS

The samples from the Rhine estuary discussed above contained 10 to 30 mg·l^{-1} of suspended material >0.5 μm. To study the effect of large particle concentrations on aggregate formation, samples were collected at three stations in the Rhine estuary where fluid mud is present. Samples were collected in the fluid mud, just above the fluid mud and in the surface water (Fig. 6). The fluid mud is formed after storms or by dredging, moves with the tides and usually is layered, which can be observed with an echosounder as well as with a gamma-ray densimeter (KIRBY & PARKER, 1977; KIRBY, PARKER & VAN OOSTRUM, 1980). The samples collected just above the fluid mud and in the surface water contained 10 to 182 mg·l^{-1} of suspended matter and the particles were of the same types (chiefly aggregates and single mineral particles) as found earlier in the Rhine estuary and the Southern Bight. The fluid mud samples contained large flocs up to several mm in diameter which were clearly visible to the eye and were connected in a very loose network. The fluid mud samples were collected with a NIO water sampler which is essentially a hollow tube that is lowered verti-

cally and is closed at both ends with lids moved by a spring that is activated by a messenger. The nature of the flocs is assumed not to have changed during this kind of sampling. With an inverted microscope the fluid mud was investigated by putting a small amount (in the order of several flocs) into a sample holder normally used for plankton counting. Even gentle stirring led to breaking up of the flocs into aggregates of 15 to 50 μm, large numbers of smaller aggregates (several microns diameter), and mineral grains. Also green plankton was found in the fluid mud (chiefly diatoms) but no other organisms apart from some bacteria. Particle size measurements were made on all the samples within a few hours after sampling. The fluid mud was resuspended by putting a very small amount in *ca* 400 ml of water with about the same salinity as the original sample. It was brought in suspension by gently stirring with the stirrer of the Coulter Counter. Later, in the laboratory, the samples were heated with H_2O_2 to remove the organic material. Heating was continued untill all H_2O_2 had been removed. The results

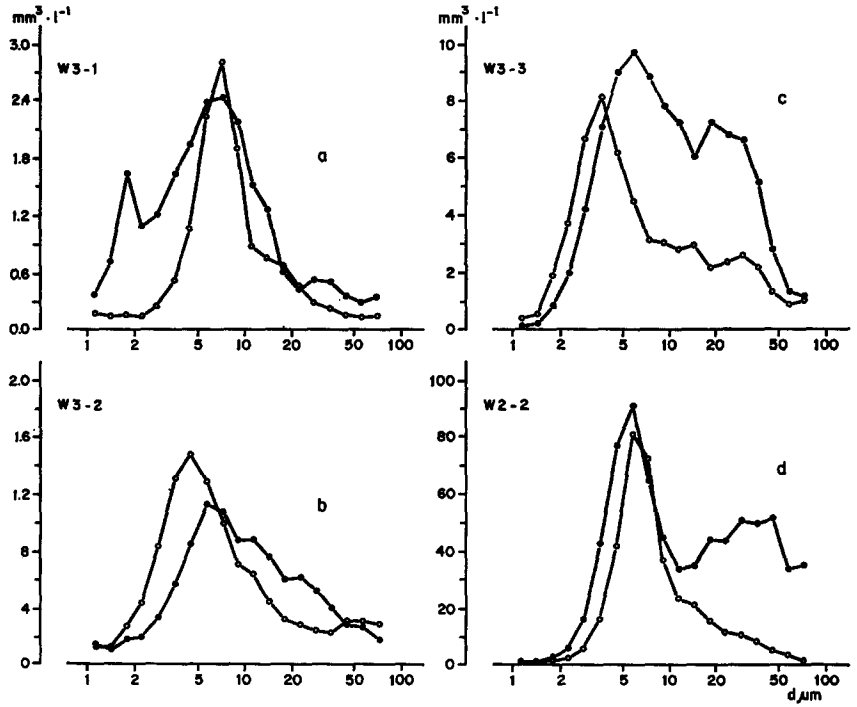


Fig. 9. Particle size distributions at stations W3 and W2, measured directly (●) and measured after treatment with H_2O_2 (○). a. W3–1 collected in surface water. b. W3–2 collected at *ca* 1 meter above the fluid mud. c. W3–3 collected in the fluid mud. d. W2–2 collected near to the bottom directly after passage of a dredger.

for all three stations were essentially the same, so only the data for station W3 are given (Fig. 9a to c). In the surface samples the suspended material was finer (Md = 4.5 to 5.6 μm) than near to the bottom (Md = 7.0 to 10.1 μm), whereas the stirred up fluid mud was slightly finer again (Md = 6.7 to 7.6 μm). The inorganic particles, however, are somewhat coarser in the surface water (for the three stations Md = 6.7 to 9.2 μm) than in the near-bottom water (Md = 5.2 to 6.3 μm) and even finer in the fluid mud (Md = 4.5 to 5.5 μm). These observations indicate that (1) the fluid mud consists of large loose flocs that easily break up when gently stirred or when resuspended (giving a suspension of predominantly particles of 3 to 10 μm with a strong admixture of larger aggregates up to 70 μm), and that (2) at high particle concentrations relatively more fine particles are present indicating trapping of fine particles in the larger aggregates or flocs. This is evident in the fluid mud. Also plankton organisms are trapped in the fluid mud and may aid in trapping finer particles by mucus secretion.

Resuspension of the fluid mud in the Rhine estuary occurs primarily by stirring during dredging; most of the mud is dredged and dumped offshore in the coastal sea. Resuspended mud was sampled at station W2 (concentration 1.4 $g \cdot l^{-1}$) directly above the bottom and directly after passage of a dredger. The size distribution of this suspension (Fig. 9d) is similar to the size distribution of the fluid mud sample resuspended in a beaker for particle size measurements and in the 2 to 10 μm range is also very similar to many size distributions found in the estuary and the Dutch coastal waters. The large admixture of coarser aggregates of *ca* 20 to 70 μm, however, has never been found in the Southern Bight or the eastern Channel. It is not clear whether these coarse aggregates break down after some time, are deposited again or whether they are reduced to low percentages by dilution. The particles (chiefly aggregates) of 2 to 10 μm are of the same type as usually found. Although it cannot be excluded that in the fluid mud stable aggregates of 2 to 10 μm are formed, it is most probable that the fluid mud flocs on resuspension break up into the original aggregates everywhere present in suspension, which, since they are glued together by organic material, have been formed through organisms.

V. SUMMARY

Particulate matter in suspension in the Southern Bight of the North Sea consists mainly of more or less round, often loose aggregates (particles glued together with organic matter) and further of single mineral grains, some small (<5 μm) chain-like aggregates, flocs sometimes containing small mineral grains and very small (<0.5 μm) organic

particles. The smallest particles observed were *ca* 0.02 μm. The average density of the particles is 1.97 and their water content 27% but there is a large variation (density 1.14 to 2.65, water content 0 to 90%) due to the mixed character of the particles and the uncertainties in estimating organic matter content.

Aggregates can be formed by:

(1) flocculation on the contact of fresh and more saline (estuarine) water,

(2) erosion of soils and consolidated fine-grained deposits,

(3) increased interparticle contact near the bottom at high concentrations of suspended matter,

(4) still larger interparticle contact during temporary deposition (during calm weather or slack tide, or accumulation in more quiet areas during storms),

(5) activity of organisms gluing particles together (by forming faeces, pseudo-faeces, or secreting mucus).

In the Rhine estuary aggregate formation on the contact of the river water and more saline estuarine water is a limited process; probably aggregates of 1 to 3 μm are formed. Aggregation by electrostatic or Van der Waals forces may occur along the entire length of the estuary but is not very important. Also there are strong indications that at low salinities oval-round particles are formed containing Ca and S and probably being a complex of Ca^{++}, SO_4^{--}, CO_3^{--} and OH^-. They were not found at salinities above 20‰ S and probably are not stable in sea water. The fact that the aggregates are glued together with structureless, often greenish or brownish substance that can be removed with H_2O_2 and therefore is assumed to be organic matter, points to aggregation by organisms or to a fresh water origin (erosion of soil aggregates). At high particle concentrations in the fluid mud that is present in the Rhine estuary large loose flocs up to several mm diameter are formed, and small particles as well as plankton cells are trapped, but on resuspension they break up into aggregates and mineral particles of predominantly 2 to 10 μm with a strong admixture of aggregates of 20 to 70 μm. The larger aggregates are not normally found in the Southern Bight in such high (relative) concentrations and probably are not stable, but the smaller aggregates are of the type normally found in suspension. It can therefore not be excluded that such aggregates are formed on resuspension of fluid mud or loose bottom deposits, although their organic content points to aggregation by organisms or in soils. The fact that flocculation on the contact of river water and estuarine water was found to be a very limited process may be caused by the pollution of the Rhine with salts, which has raised the salinity of the river to an average of 0.61‰ S (maximum 0.91‰ S).

It follows from this discussion that the aggregates in suspension in the Southern Bight of the North Sea are likely to be of multiple origin but predominantly formed by organisms. A multiple origin is also implied by the multiple origin of the material in suspension as a whole which is chiefly supplied from the Channel, from rivers and from seafloor erosion with additional amounts from coastal erosion, primary and secondary production and the atmosphere.

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